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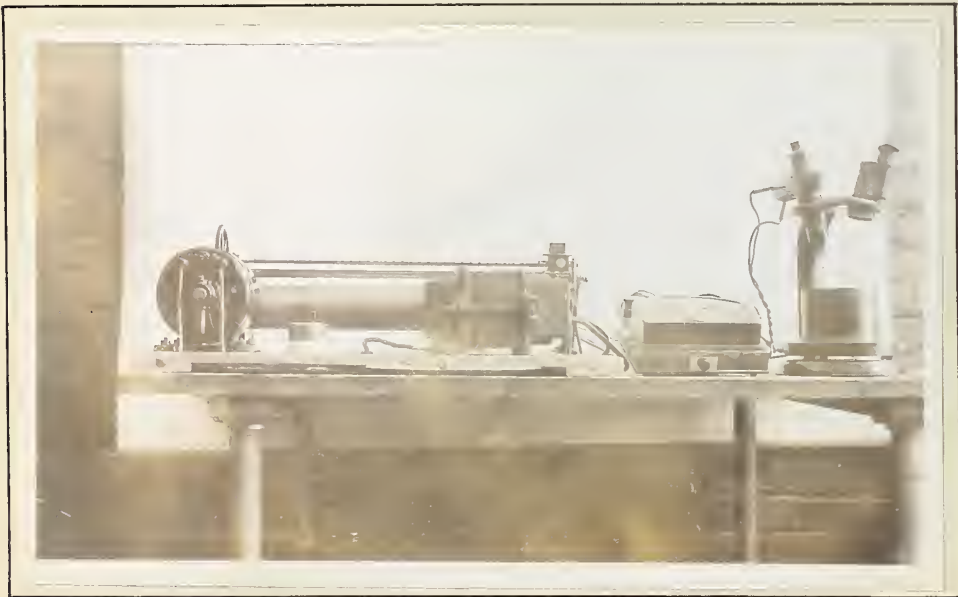
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Top View



Side View

The De Graaf Apparatus

RELATIONSHIP OF THE DEGREE OF GRAIN ORIENTATION APPEARANCE
AND OF FOLDED SURFACES AND SURFACES TO
STRUCTURE OF SILICATE MINERALS.

-by-

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A THESIS

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3

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CONTENTS

PREFACE AND ACKNOWLEDGMENTS	Page
INTRODUCTORY	I
PART I	
THE DE GRAAF 154 FUSION APPARATUS; ITS CALIBRATION AND USE IN DETERMINATION OF MELTING POINTS OF SILICATE MELTS.	
CHAPTER I DESCRIPTION OF APPARATUS	
Heating Chamber	8
Power Unit	9
Temperature Measurement	10
CHAPTER II PREVIOUS WORK	
Historical	11
Selvig	12
Fitterer and Royer	13
Conclusions from Previous Work	18
CHAPTER III STANDARDIZATION OF THE INSTRUMENT	
Introductory	20
Calibration	20
Black body conditions	21
Glass Window Correction	23
Calibration Curve	26
Cap and Window Correction Tests	28
Lag Effect on a Rising Cycle	33

	Page
CHAPTER IV MELTING POINT DETERMINATIONS	
Introductory	37
Pure Substances	37
Coal Ash	38
Orton Cones	43
Slags	47
CHAPTER V CONCLUSIONS	52

PART II

CRYSTALLIZATION IN SILICATE MELTS; INTERPRE-
TATION OF CRYSTAL STRUCTURE DEVELOPED AND
DETERMINATION OF MINERAL ENTITIES BY POLISHED
SECTIONS AND BY THIN SECTIONS.

CHAPTER I INTRODUCTORY AND PREVIOUS WORK	
Introduction	56
Previous Work	56
Geological Approach	57
Metallurgical Approach	58
McCaffery's Work	60
CHAPTER II PREPARATION AND CRYSTALLIZATION OF THE SLAGS.	
Synthetic Slags	63
slag A	64
slag B	65
Metallurgical Slags	66
slag C	67
slag D	68

CHAPTER III MINERAL CONSTITUENTS OF THE SLAGS

Introduction	71
Slag A	76
Slag B	82
Slag C	83
Slag D	84
Slag E	85
CHAPTER IV CONCLUSIONS	87

BIBLIOGRAPHY

ILLUSTRATIONS

LIST OF ILLUSTRATIONS

PART I

Figure		Page
	The De Graaf Apparatus	(Frontispiece)
1	Optical Pyrometer	(Facing) 20
2	Standard Ash Fusion Furnace	(Facing) 20
3	Calibration Curve of the Apparatus	27
4	Relation between Calibration Curve and Black Body Check Determinations	32

PART II

Figure		Page
1	McCaffery's Tetrahedron for $\text{CaO}, \text{MgO}, \text{Al}_2\text{O}_3, \text{SiO}_2$	90
2	Surface Appearance of Slag A	91
3	Vertical cross-section of Slag A	91
4	Polished Section, Slag A; Top of melt (HCl etch)	92
5	Peg Structure, Slag A; (HCl etch)	92
6	Polished Section, Slag A; Top of melt (HF etch)	93
7	Thin Section, Slag A; Top of melt, crossed nicols	93
8	Polished Section, Slag A; Center of melt (HCl etch)	94
	Thin Section, Slag A, Center of melt, crossed nicols.	94
10	Polished Section, Slag A; Center of melt (HCl etch)	95

Figure		Page
11	Polished Section, Slag A; Bottom of melt (HCl etch)	95
12	Thin Section, Slag A; Bottom of melt, crossed nicols	96
13	Polished Section, Slag B	96
14	Polished Section, Slag B; (HCl etch)	97
15	Polished Section, Slag C	97
16	Polished Section, Slag D, as received	98
17	Polished Section, Slag D, recrystallized (HCl etch)	98
18	Polished Section, Slag E, as received	99
19	Polished Section, Slag E, recrystallized (HCl etch)	99

INTRODUCTORY.

The De Graaf apparatus is a compact and relatively simple piece of equipment developed for determinations on fusion points of coal ash and similar silicate mixtures. It allows of close temperature control of small quantities of materials and for variations in atmospheric conditions of the tests. Observations on physical changes during the progress of the melting operations are made through a microscope and thus the complete test is under close observation at all times. The resultant liquids cannot be contaminated by reaction between the melt and the containing vessel. The rate of heating or cooling may be controlled at will and the test held at any given temperature within relatively narrow limits for any length of time. Thus the variables, temperature, time and furnace atmosphere are all subject to close control, and, within limits, pressure also. The apparatus should be adaptable to studies on certain of the phase changes occurring in complex mixtures such as are present in metallurgical slags and other products.

Much work has been done by many investigators on

the thermal characteristics of binary, ternary and quaternary mixtures of silica and metallic oxides. These have determined the constitution diagrams on biaxial tri-axial and tetrahedron figures for various mixtures of silica with lime, magnesia, alumina and ferrous iron. Little attention has been given to mixtures containing other bases. Modern metallurgical slags, particularly those of copper and lead smelting, contain, besides the bases listed above, oxide of zinc (ZnO) and the higher oxides of iron, ferric (Fe_2O_3) and ferroso-ferric (Fe_3O_4) and these substances play an important part in the melting and free running characteristics of the slags. The thermal characteristics of these five and six component slags are not readily amenable to co-ordinate delineation and they must be studied individually and collectively as impurities in or mixtures with binary, ternary or quaternary mixtures of the principal slag forming ingredients. The number of experiments thus involved is tremendous and any apparatus which would facilitate the experiments would greatly lessen the labor involved. The relative ease with which fusion points may be determined with the De Graaf apparatus should prove a great help in this respect.

The investigations reported in this Thesis were undertaken in the hope that the De Graaf apparatus could be adapted to studies on the thermal characteristics of complex mixtures of silica (SiO_2) and numerous metallic bases such as are met with in metallurgical slags. The work was designed to consider both the question of slag formation in mechanical mixtures of the slag forming ingredients and the determination of the temperature at which or the temperature range through which melting or freezing of the previously formed slag occurs. The work was also planned to include microscopic studies on thin sections and polished sections of the solidified slags for determination of the mineral constituents developed.

The De Graaf apparatus has not received ready recognition by testing and research laboratories doing coal ash fusions and similar work. Fusion point determinations made with the apparatus have not checked with determinations made with the American Society of Testing Materials Ash Fusion equipment and methods and the reasons for the differences have not been developed. Usually duplicate tests on the same apparatus will check but there is no obvious relationship between the temperatures given by the apparatus and those obtained by

standardized methods or by other De Graaf apparatus on the same materials. Some laboratories report that multiple checks on the same material can be obtained by different observers; others claim that no reliability can be placed on the results of observations unless they are all made by the same observer. Apparently each unit has its own characteristics and idiosyncrasies which have to be established and known by the investigator.

The particular De Graaf apparatus used for these investigations was loaned by the Fuels Division of the Research Council of Alberta. It was originally obtained for ash fusion determinations in the routine laboratory work of the department but had not been found satisfactory in that determinations made by it did not and could not check with determinations made on the same materials with the A.S.T.M. standard equipment. The apparatus had not been standardized either as to accuracy or as to method of operation. Thus the first objective of the investigations became the determination of a calibration curve for the instrument. This calibration curve had to satisfy not only fixed points such as the melting points of pure substances, chemical compounds and eutectics but also the temperature ranges of melting or

solidification of mixtures. It is believed that a satisfactory calibration chart has been obtained but the work proved laborious and time consuming and little opportunity was found for investigations on the actual application of the apparatus to the general problem of slag formation and slag fusion temperature determination. A start, however, has been made and it is hoped that the work so far done will form a basis for more extended investigations by another investigator at a later date.

It has been found impossible to use portions of the solidified melts from the De Graaf fusion determinations for microscopic examination. Upon solidification the fused mixture adheres firmly to the platinum strip and no way short of solution of the mass will allow of its removal without destroying the platinum strip. Some samples for microscopic examination have been prepared by melting mixtures in a graphite lined fire clay crucible in the standard ash fusion furnace, controlling the temperature of the melt and the rate of cooling by observation with an optical pyrometer at temperatures previously determined by the De Graaf apparatus. The samples are thus not identical with the melts made on

the platinum strip of the De Graaf apparatus and there has been some chemical change due to contact with the container wall or lining. The results of these observations are given more to indicate the nature of the mineral constituents and the microstructures that may be expected in metallurgical slags than to indicate the actual conditions resulting in fusion and solidification of the mixtures studied.

PART I

THEORY OF FUSION; ITS QUALIFICATION
AND USE IN DETERMINATION OF MELTING POINTS OF
SILICATE BODIES.

CHAPTER I

DESCRIPTION OF APPARATUS

The De Graaf (1) Apparatus (see frontispiece) is built in three parts; the furnace, the power unit and the millivoltmeter by means of which temperature measurements are made.

Heating Chamber.

The heating chamber consists of a heavy brass base over which is placed a brass cap fitting into a groove in the base. A heavy grease spread on the gasket which is placed in the groove will maintain air-tightness. The top of the cap is fitted with a clear glass window with ground fittings, and through this the fusion of substances within may be watched.

The heating element is a platinum strip, suspended between two posts which project from the base of the heating chamber, and are covered by the cap. The platinum strip is 2.5 inches long, 0.54 inches wide and 0.0005 inches thick. This platinum strip serves as the heating unit for temperatures up to 2820°C ., above that temperature similar strips made of molybdenum may be used to a temperature of 3650°C .

Power Unit.

The platinum strip is heated by means of an electric current supplied by the power unit. Current from a 110 volt lightning circuit is passed through a transformer, where it is reduced to 10 volts, and this, after passing through a rheostat, is admitted to the heating chamber.

The rheostat controls the current to the platinum strip, and temperature changes are obtained by adjusting the rheostat resistance. This can be done by hand, or automatically by means of a screw driven by an electric motor. Thus the motor, which is placed in parallel with the heating circuit, automatically decreases the rheostat resistance and raises the temperature of the platinum strip in a gradual and regular manner. The feed screw is so threaded that the current is increased rapidly up to a temperature of 2200° F. and from this temperature the current is increased more slowly, so the rate of change of temperature with time is correspondingly decreased. If required, the platinum strip can be held at any desired temperature by disengaging the small pin which connects the rheostat rider to the feed screw.

The specimen is placed in the center of the platinum strip. It is observed by means of an adjustable

Teiss microscope, mounted on a frame above the window. The microscope is fitted with a smoked glass eyepiece, and has a magnifying power of about 9.

Temperature measurement.

The temperature is measured by a Siemens-Helmholtz pyrometer (10) a special type of radiation pyrometer. The current generated in the thermocouple deflects the needle of a Leeds and Northrup millivoltmeter. For convenience in observation the millivoltmeter is graduated in temperature units (degrees F.) and temperature readings are thus read direct from the instrument.

The heating chamber is equipped with inlet and outlet tubes so that any desired atmosphere conditions may be established within the chamber.

The whole apparatus, heating element and chamber and temperature indication device in the literature has been called a micropyrometer, and the method of temperature measurement is called fusion point investigation.

CHAPTER II

PREVIOUS WORK.

History

The most complete publication on the use of the micro-pyrometer for high melting point investigations is the bulletin by Fitterer and Roger (2). The first micro-pyrometer was made by Burgess (3 & 4), and used to investigate refractory oxides of high melting point. Results were accurate to within a few degrees centigrade.

Fieldner and Selvig used a modification of Burgess' apparatus in coal ash work for some years. Selvig (5) mentions the use of a polyduran coil of wire, built with brick outside to hold the heat, and with the sample, a cone, placed inside the coil. Temperature measurements were by means of an optical pyrometer.

Fieldner, Selvig and Parker (6) used an instrument much like the De Graaf fusion furnace but measured the temperature of the platinum strip by means of an optical pyrometer. They found that for most coals a softening point under 2500° F. by the gas furnace method could be checked within 100° F. by the micro-pyrometer method, if similar atmospheric conditions were maintained for the

two determinations. For higher softening temperature coals, the micropyrometer method tended to give considerably lower results. They concluded that the two methods could not be considered strictly alternative for all coal ashes. Checks between different laboratories indicated that the micropyrometer method could check itself as closely as the gas furnace method.

Herty and Fitterer (7) used a micropyrometer for their investigations of the Ferrous-oxide Silica system. They first calibrated their instrument over a wide range. The samples were then melted in a nitrogen atmosphere. Excellent checks were made in these determinations.

Selvig

In 1929 Selvig (8) conducted some investigations the purpose being

"to determine how closely different laboratories can check one another in making determinations of fusibility of coal ash with the De Graaf electric coal-ash fusion furnace, how well duplicate determinations by the same laboratory will check, and how the results with the De Graaf furnace compare with those of the standard gas furnace method of the American Society for Testing Materials."

From this investigation Selvig concluded:

(1) that the ability of the same laboratory to check itself varied considerably; in some cases checks

within 30 °, were obtained, but in other large differences occurred; (2) determinations made by different laboratories showed wide differences in the fusibility of the same coal ash; (3) a comparison of fusibility results by the De Graaf method and the standard gas furnace method showed poor agreement.

Fitterer and Royer.

The strongest defenders of the case of the micro-pyrometer, as opposed to the standard gas furnace method of determining melting points, are Fitterer and Royer (2). These authors begin their report with a discussion of melting points, and from their report the following points seem of importance:

"At the melting point of any substance, a certain amount of solid must be present so as to establish this equilibrium. It is the mistaken idea of some that the melting point is that point at which the solid phase completely disappears."

.....
"It is well known that crystals are not necessarily solid, nor is a solid necessarily a crystal. Liquid crystals are known and accepted by most scientists, as also are the conceptions of the amorphous state, particularly in the case of silicates or glasses.....Liquids are capable of undercooling so that there may seem to be no lower limit to the liquid state, unless it be absolute zero..... Gosman states that the melting point of silica is difficult to determine because the material does not flow when a crystal melts, and the fragments retain their original shapes and positions, due to the high viscosity of the liquid silica."

After a careful consideration of the melting points of silicates, the authors define the melting point of refractory materials as follows;

"The melting point of an irregularly shaped refractory particle is that temperature at which the viscosity (or crystalline rigidity) is overcome by the random motion of the molecules, and at which the surface tension is sufficient to draw the particle into a globular shape."

The author goes on to state that this observed melting point is not to be confused with the "softening" point. Some materials which have a wide range of heterogeneous equilibrium do not melt sharply. Instead, a small amount of liquid first appears (softening point, see p. 12) which gradually increases until the last portion of solid disappears. The temperature at which there is a very small amount of solid remaining is the melting point and may be observed as described by the above definition. The softening point is observed to be that temperature at which the corners of an angular piece of the solid substance first become rounded. Both of these points may be experimentally checked.

In commenting on Selvig's (8) conclusions regarding the erroneous results obtained by using the micrometrymeter, Fitterer and Royer say,

".....The gas furnace

method is so insensitive that it does not detect (a) the effect of the sample, being a mechanical mixture of various refractory oxides; and (b) the effect of the reduction of the oxides with a 2:1 CO-CO₂ atmosphere. In other words, the gas furnace simply determines an over-all sintering-fusion point. It is quite likely that if a given globule obtained from the fusion of a cone in a gas furnace were powdered and remelted in the micropyrometer, check determinations would be obtained. Hence no one should attempt to determine the melting point of a mechanical mixture of oxides by the micropyrometer method. Widely varying results are to be expected. However, if the mixture has been previously fused to ensure homogeneity and then powdered and sized, very satisfactory determinations may be obtained."

Fitterer and Royer describe briefly their procedure in determining a melting point. Pure oxides, stable compounds and eutectic materials offer no great difficulties. A few grains of 130-150 mesh sized material is placed in a slight depression which has previously been made on a platinum strip, the cap is placed on, the desired atmosphere obtained and then the current turned on. The melting temperature is read when the particles assume a globular shape, as is explained in their definition of melting point.

They state that the chief advantages for the instrument for such materials as FeO, MnO, 2FeO.SiO₂ etc., lies in the elimination of refractory difficulties and in absolute control of atmospheric conditions. The

real difficulties are encountered when studies are made of slag systems which have unstable compounds, liquid phases of high viscosity etc.. Such difficulties, they believe, would be just as great or greater in other methods.

For samples which are not single oxides or compounds two transformations are observed, according to these authors. One represents a noticeable softening of the sample which probably corresponds to the eutectic temperature, and the second is that point at which the material is completely molten as closely as can be determined by observation. Where the difference between these two points is small (not over 150°C.) the two changes are easily discernible. Where the softening interval is large transformation is sluggish and it is exceedingly difficult to determine by observation the exact points at which the last trace of solid becomes fluid.

These authors also give some precautions which are of considerable importance, if good results are to be obtained using the De Graaf apparatus.

"On each determination, duplicate conditions must be maintained; such as the rate of flow of gas through the chamber; the rate of heating of sample; and proper focusing of the radiation pyrometer for

temperature measurement.

"A slow heating rate is essential for two reasons: (1) To enable the temperature of the sample to keep pace with that of the platinum strip and (2) to allow the recording galvanometer to follow at the same rate.

"A fast heating rate results in the strip's temperature being continually higher than that of the sample, even in the minute sample used, because of its low heat conductivity. Also a fast heating rate causes the indicating needle of the millivoltmeter to lag behind the true value, because of its inertia.

"The sample in which melting points are to be determined must be placed on a clean area of platinum strip for each determination.....

".....To prevent the formation of an interfering film on the quartz window in the chamber cell, it must be removed and cleaned before each melting point determination.

"Any change in the distance between the strip and thermocouple affects the temperature readings materially....."

Two sections of the summary of Vittoria and Goerke (2) report give their opinion as to the usefulness of the thermocouple method of melting point investigation.

"The method is very accurate for the determination of the melting points of simple compounds, eutectics and pure alloys. It can be used for materials which present insurmountable difficulties for atomic absorption spectroscopy but other more widely known procedures.....

"The accuracy of the method is admittedly increased in the study of materials which have similar temperature ranges of solid-liquid insolubility.

Also, for materials such as the authors have investigated there is no other method which shows greater accuracy."

Conclusions from Previous Work

The De Graaf apparatus in its essentials is not a new instrument, the principles having been used by various investigators since 1907. To some of them, especially Fitterer, it has proved a very useful instrument, as accurate as any other type of melting point apparatus for some purposes. At one time it was suggested that it, as well as the gas furnace method, be adopted as a tentative standard in coal ash work. It is interesting that Selvig, as well as Fitterer, was one of the individuals who made this proposal. The instrument was successfully used in determinations of the ferrous oxide-Silica system by Hertz and Fitterer and their report is accepted and referred to in many articles involving this system.

Selvig's (8) report showed that the design of the De Graaf instrument and its method of operation as laid down by the manufacturers would not give consistent results. This is due to (a) improper calibration of the instrument and (b) incomplete definition of the softening and fluid temperatures as shown in the De

Grass apparatus. The first of these is inherent in the instrument itself and involves the relationship between electric potential developed by the Ardrometer and temperature. The millivoltmeter of the instrument is graduated in temperature units and as will be shown later, these are not true temperatures. The second depends upon the observer and his interpretation of these temperature points. The instrument is sensitive to all variations of the material of which the melting point is being determined. Some isolated particles will melt before the main mass; others may remain solid several hundred degrees after the main mass is fused. The condition of the mass as representative of these particular temperature points has to be standardized.

Witterer and Royer (2) have determined the best practical uses of this type of apparatus and their report treats the method more fairly than any other that has come to the attention of the author. They define the melting point to be used. They state the necessity for standardizing the instrument, and give a method of doing this. They sum up the applications of the instrument. Witterer has used the instrument in a variety of investigations and is convinced of its usefulness.

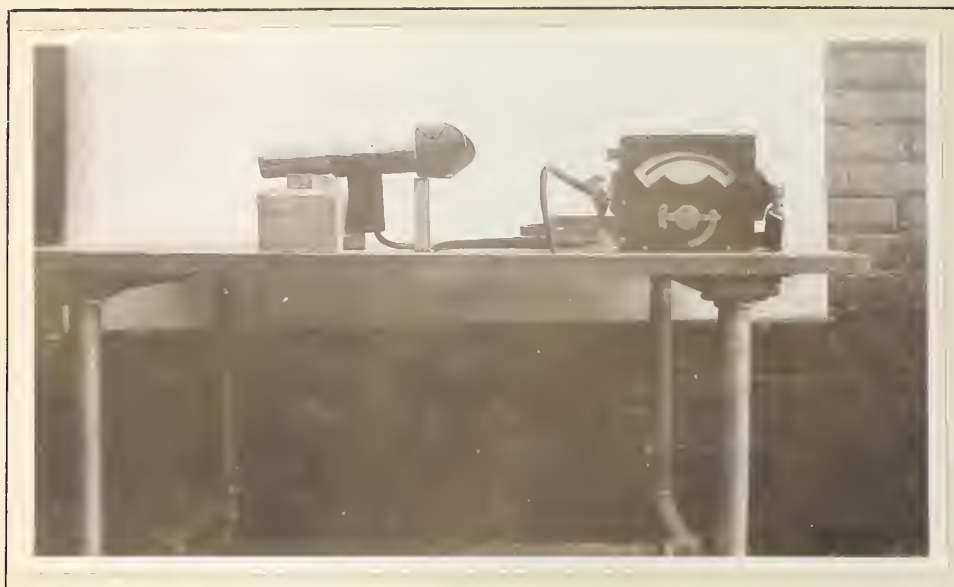


Figure 1.
Optical Pyrometer.

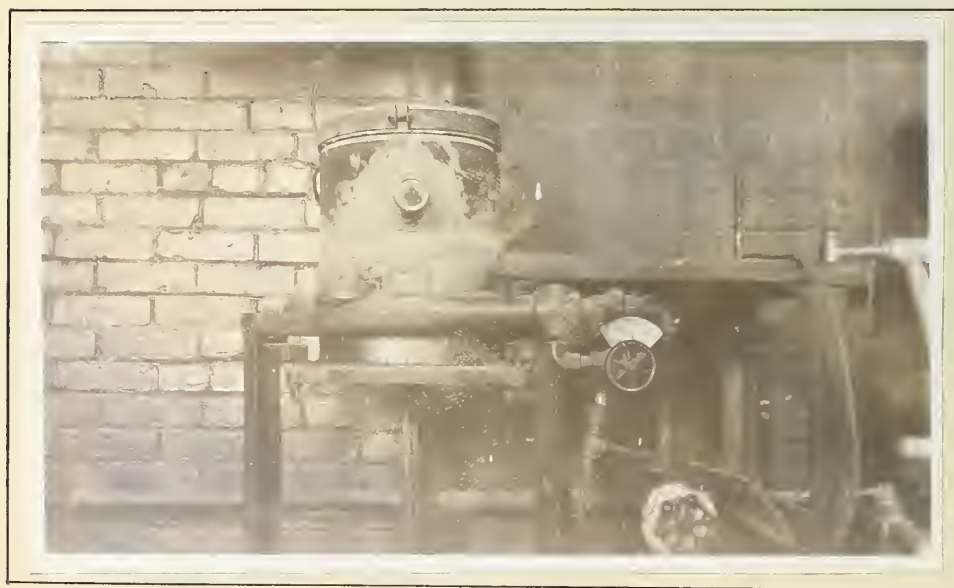


Figure 2.
Standard Ash Fusion Furnace.

GILBERT III

STANDARDIZATION OF PTL INSTRUMENT

Introductory

One of the chief reasons why the De Graaf has not proved a useful instrument is that it is not properly calibrated. The scale on the millivoltmeter supplied is graduated to be read in degrees Fahrenheit, but it is not a correct temperature reading. Before the instrument can be used it is necessary to have a scale or a graph, by means of which observed temperatures may be converted to true temperatures.

In the present investigations the De Graaf apparatus has been calibrated against a Leeds and Northrup optical pyrometer the calibration of which had been checked in the laboratories of the Research Council of Alberta.

Calibration

Calibration of the De Graaf was made in the following manner: The De Graaf instrument was brought up to a temperature of approximately 1650°P., as read on the millivoltmeter. The rider on the rheostat was disengaged and the temperature allowed to become steady.

The optical pyrometer was then aligned through the opening usually occupied by the microscope. When the optical pyrometer was properly focused on the hottest part of the platinum strip, the temperature was read simultaneously on the optical pyrometer and the thermometer by two operators.

Black Body Conditions.

The optical pyrometer readings thus obtained do not represent the true temperature. Optical pyrometers are designed for black body conditions and these conditions are realized in the chamber of the De Graaf apparatus. A correction for black body conditions has to be applied, as noted by Foote, Fairchild and Laurison (2), the optical pyrometer measures the intensity of the radiant energy which the hot body emits, referred to a restricted portion of the visible spectrum. In general, the intensity of radiation depends not alone upon the temperature of the source, but also upon the particular material constituting the source. Thus, for example, carbon appears to be about three times as bright as platinum when both are at the same temperature. This is expressed by the statement that the emissive power of carbon is about three times that of platinum.

material having the highest theoretical emissivity is 1. Hence all other materials have emissivity less than 1.

Platinum does not oxidize readily. Its surface remains clean and bright. Hence its emissivity will remain constant. Knowing the emissivity it is possible to construct a table showing the correction to be applied to optical pyrometer readings when used to measure temperatures in other than black body conditions. Table III. 1 shows these corrections as determined by Foster, Fairchild and Harrison.

That such a conversion is possible is borne out by the fact that an optical pyrometer has been used to maintain exact temperatures of platinum catalysts used in the industries as a catalyst. This involves a second conversion, due to the fact that the instrument is being used on the catalyst instead of a black metallic surface, but the correction has been evaluated and has worked as is desired.

Table I.

True temperature versus observed temperature measured by standard pyrometers using red light ($\lambda = 0.65 \mu$) when sighted upon platinum in the open. Columns one and two taken from Foote, Fairchild and Harrison. (9)

Observed temperature °C.	True temperature °C.	Observed temperature °F.	True temperature °F.
700	750	1292	1382
800	861	1472	1582
900	975	1652	1782
950	1020	1742	1886
1000	1067	1832	1989
1050	1114	1922	2091
1100	1202	2012	2198
1150	1290	2102	2300
1200	1320	2192	2408
1250	1371	2282	2507
1300	1465	2372	2615
1400	1555	2552	2831
1500	1675	2732	3047

Glass Window Correction

The presence of the sapphire sighting window in the opening of the chamber necessitates a further correction. The amount and sign of this correction has been determined by Foote, Fairchild and Harrison (9). The presence of the window results in a lowering of the intensity of the light emanating from the source and thus the correction is always positive. Table 2, from

Boote, Fairchild and Harrison, indicates the amount to be added to optical pyrometer readings for a single clean glass window.

Table 2.

Correction to observed Temperatures for Absorption of Light by a Single Clean Window. Centigrade readings from Boote, Fairchild and Harrison. (9)

Centigrade		Fahrenheit	
Observed Temperature	Correction Temperature	Observed Temperature	Correction Temperature
600	5.5	1110	3.2
800	5.4	1470	9.7
1000	6.0	1830	14.4
1200	10.0	2190	18.0
1400	13.0	2550	22.0
1600	16.0	2910	29.0
1800	20.0	3270	36.0

Table No. 3 shows the temperature observations made in the calibration of the De Graaf apparatus. Column 1 gives the temperature as read from the De Graaf millivoltmeter and column 2 the temperature equivalent of the millivolt reading of the optical pyrometer. Column 3 shows the optical pyrometer temperature after applying the correction from Tables 1 and 2.

Table 5.

Comparison of Temperature Observations by De Graaf Apparatus and Optical Pyrometer.

De Graaf Temperature °F.	Optical Pyrometer °F.	Optical Pyrometer Corrected °F.
1625	1685	1818
1680	1714	1855
1795	1800	1953
1840	1848	2006
1920	1890	2056
2050	2025	2212
2090	2060	2252
2140	2104	2305
2190	2152	2360
2250	2193	2415
2240	2220	2438
2260	2246	2471
2500	2274	2499*
2300	2316	2559
2315	2346	2588
2320	2282	2508
2350	2346	2588
2365	2380	2619
2375	2375	2618
2420	2390	2633
2470	2450	2706
2540	2514	2783
2570	2549	2826
2610	2570	2851
2630	2600	2886

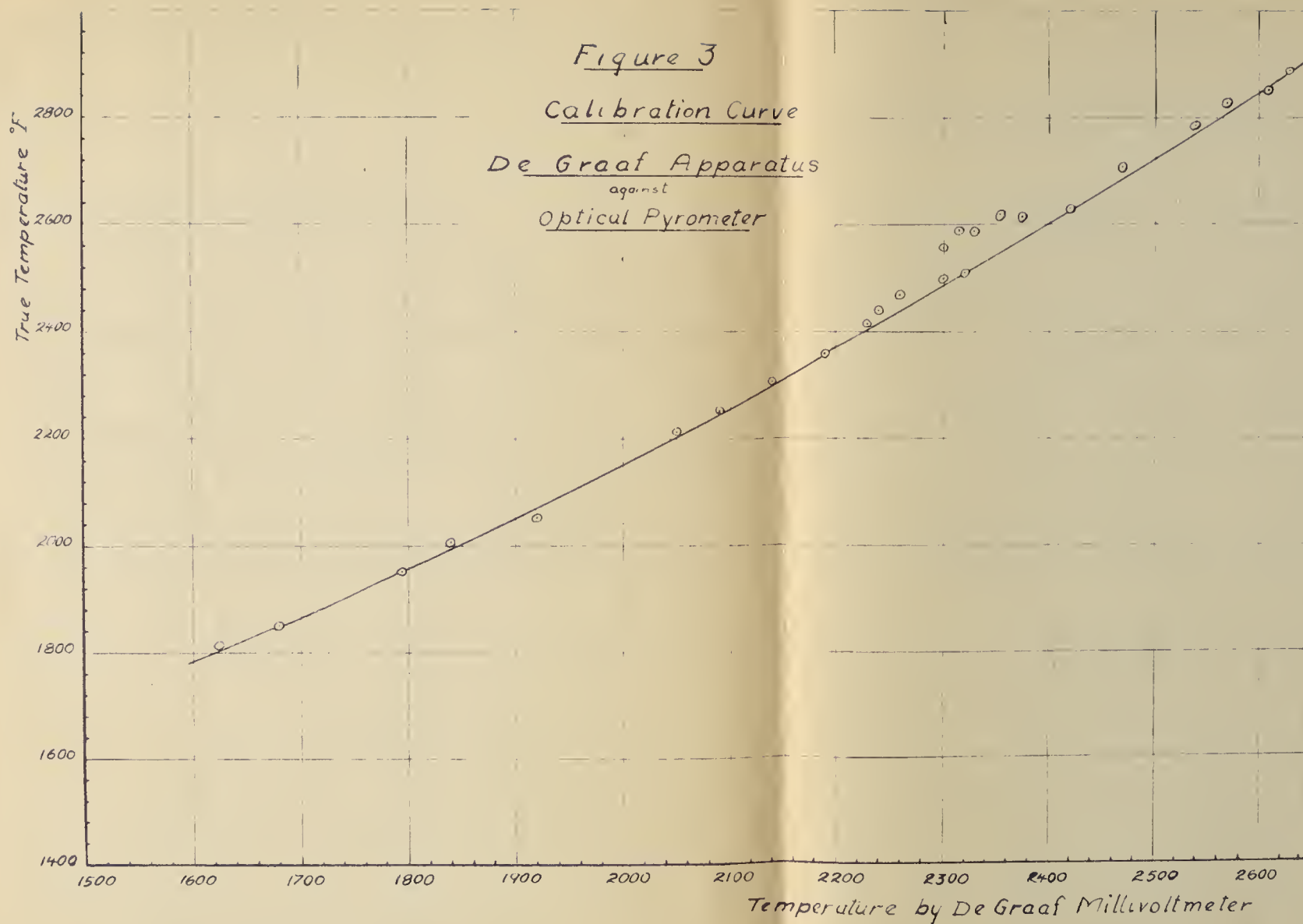
* The variation here cannot be accounted for.

Calibration Curve

Figure 5 is a plot of the figures shown in Column 1 and 5 of table No. 3. It is thus the calibration curve of the apparatus.

The resulting curve is not a straight line. Pitterer and Royer (2) found that the curve of true temperature against millivoltmeter readings was a straight line. Presumably, the manufacturer of the De Graaf has worked out theoretically the relation between temperature and millivolt readings for this instrument, and has substituted the temperature scale for the millivolt scale on the millivoltmeter. It is also possible that a delicate instrument like the Ardrometer is not amenable to this standardization. However, the Stefan-Boltzman law will still apply, so that a straight line relation should exist between readings given by the De Graaf, and true temperature.

The curve of Graph 1 is not far off a straight line, and the question arose as to whether or not to plot it as the best straight line, or as a curve. The curve was chosen, as is shown. Had the exact law on which the De Graaf temperature scale was based been supplied with the instrument, it might have been possible to



determine the exact shape of the curve from theoretical considerations. Since no such information was known, a curve based solely on experiment was considered advisable.

Can and Window Correction Tests.

Some tests were made to find the influence of the supposed black body conditions which are obtained in the blackened chamber, on the readings of the instrument. Two runs were made using both the pyrometer and the Ardometer to measure the temperature. The first run was made with the can entirely off the furnace, so the platinum strip was in the open. The second was made with the can on, but the pyrex glass window taken off. In both cases there were no readings taken through the glass window, and temperatures observed by the optical pyrometer had only to be corrected for black body condition, by interpolation of Table 1. These results are given in Table 4, and the points plotted in Figure 4. The curve in this figure is the same as that shown in Figure 3.

The second column in Table 4 gives corrected De Graaf apparatus readings. If the blackened interior of

the cap of the apparatus contributes nothing at all to black body conditions then readings taken without the cap on should be just as suitable for standardization purposes as those with the cap in place. There are several reasons why it was considered inadvisable to use these figures in the actual calibration. In the first place, air currents changed the temperature of the string suddenly, so that it was difficult to maintain steady conditions. Further, the absence of the glass window, and of the furnace cap, affected the Ardometer reading. If a fairly uniform temperature reading was obtained with the cap off, suddenly replacing the cap without the glass window would raise the De Graaf temperature reading 10° - 15° F. If now the glass window was to be put on, the temperature dropped 80° in the lower ranges up to 2300° F., and 100° in the upper ranges, above 2400° F. Millivoltmeter readings given in column 2, Table 4, have had this latter correction applied.

In other words, a window correction is necessary for the Ardometer, of the same nature as that for the optical pyrometer, shown in Table 2. The De Graaf reading for the first observation shown in Column 2 is 1725° F., with cap off and no glass window intervening

between the Ardometer and the platinum strip. To make this reading comparable with observations made with the glass window intervening, a correction of -80°F. must be made, which would give a temperature reading of 1645°F. For a reading of 2550°F. the correction would be -100°F. and the temperature 2450°F.

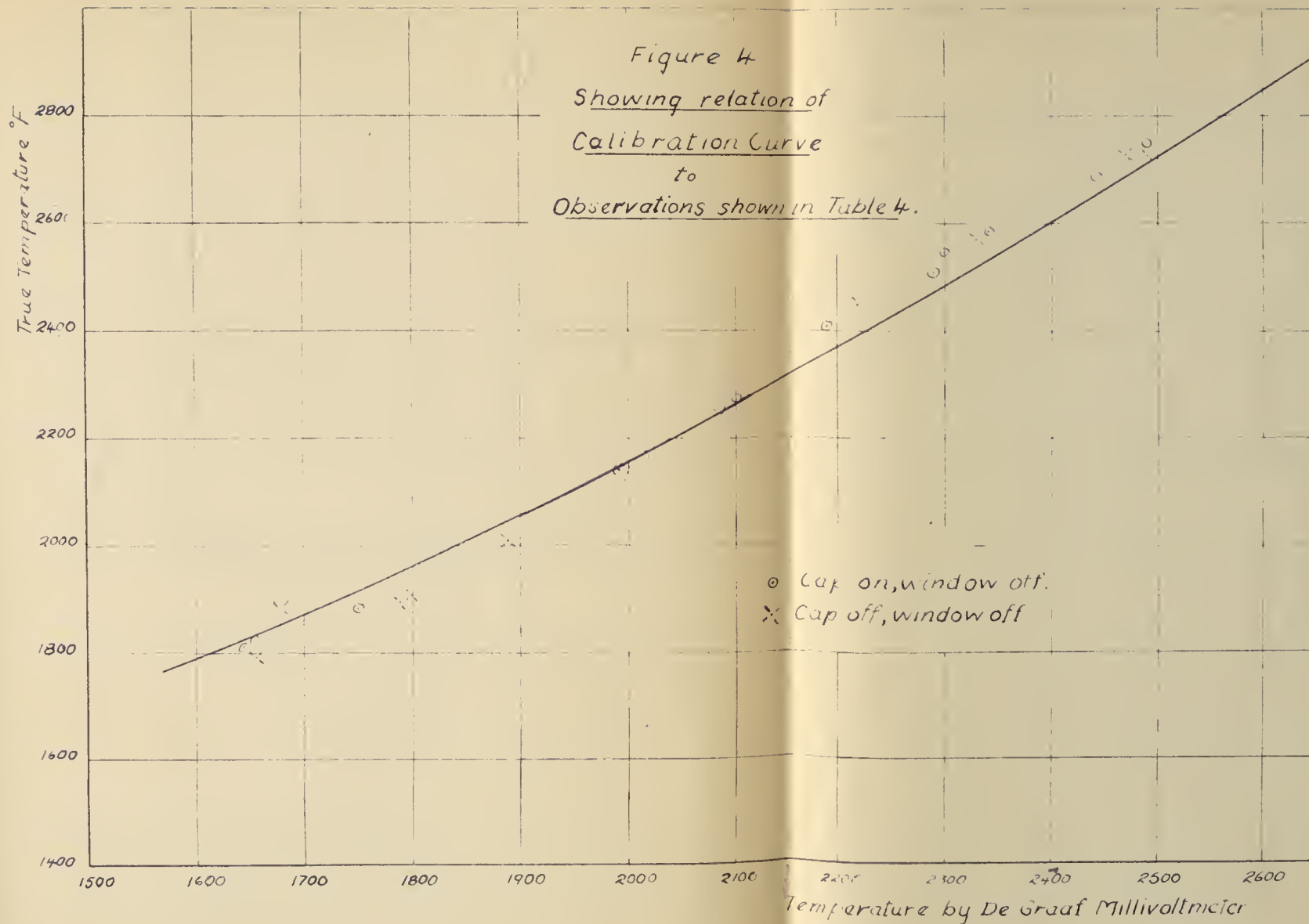
Replacing the cap without the glass window as mentioned above, would of course to a large extent restore the black body conditions which this determination was to eliminate. However the only effect is to raise the temperature $10^{\circ}\text{-}15^{\circ}\text{F.}$, by decreasing the air currents and by keeping the platinum strip in an atmosphere of warm air. This rise in temperature will be shown by both optional pyrometer and Ardometer and will not affect the calibration. It should be noted that this test in itself proves that black body conditions are not being obtained in the heating chamber.

The observations of Table 4, plotted in Figure 4 indicate that the cap has no appreciable effect on the readings of temperature as recorded by the optical pyrometer or by the millivoltmeter. It does not contribute to the black body conditions which are considered necessary for correct readings with either

Table 4.

	Temperature by De Graaf °F.	Same corrected for window °F.	Optical Pyrometer Temp. °F.	Corrected for Black body conditions °F.
Cap off, window off.	1725	1645	1665	1797
	1750	1670	1710	1846
	1860	1780	1753	1898
	1870	1790	1767	1914
	1960	1880	1847	2006
	2070	1990	1968	2141
	2090	2010	1986	2167
	2160	2080	2055	2238
	2293	2213	2234	2454
	2411	2310	2330	2567
	2550	2450	2470	2735
	2570	2470	2470	2755
Cap on, window off.	1725	1645	1680	1813
	1735	1655	1695	1830
	1830	1750	1739	1869
	2075	1996	1968	2148
	2145	2065	2070	2265
	2180	2100	2080	2276
	2270	2190	2190	2410
	2380	2290	2272	2518
	2402	2300	2318	2547
	2440	2340	2344	2585
	2590	2490	2505	2753

instrument. It appears that it is possible to consider a reading made sighting on the platinum strip as equivalent to sighting on a wall of bright platinum,



in which case the results given in Table 2, Harrison (3) and April.

The relations recorded in Table 2 give a smooth curve up to temperatures ranging from 2500° to 3000° K. In this area the plotted points are rather irregular, usually too high. An attempt was made to extend the curve at this point, but this was unsatisfactory. The difficulty seemed to be one of obtaining the correct optical pyrometer readings. Much care was necessary to get the loop of the filament to disappear in the usual manner. However, as mentioned before, if the De Graaf has been calibrated on a theoretical background, (using the Stefan-Boltzmann Law) and mathematical relations should exist between the observed temperature and the true temperature. The curve correlating the two temperatures should be simple and continuous. It should exhibit no irregularities. Consequently it is believed that the relation shown by the graph will be nearest correct.

Log Effect on a Rising Scale

The De Graaf temperatures and corresponding optical pyrometer readings shown in Table 2 were obtained while the technician stopped and after conditions had become relatively steady. Usually, however, the instrument

is read on a rising cycle. At the temperature of reading there may be a difference between the temperature indicated by the Ardoneter-millivoltmeter and the actual temperature of the platinum strip upon which the observations are made. The magnitude of the difference is shown in Table 5.

Table 5.

Temperature of Disengagement °F.	Temperature reached by needle °F.
1600	1675
1700	1770
1800	1870
1900	1990
2000	2065
2100	2115
2200	2210
2300	2310
2400	2412
2500	2510

The table shows that up to a temperature of 2000°F. the final temperature is approximately 70° above the original. Above 2000°F. it is on the average 10° above the original.

The significance of the spread between the two

readings is not entirely clear. At least two factors enter into the lag which the instrument readings show. One is due to the lag of the Ardometer, which when focused on a body takes eight seconds (10) to come to the temperature of that body. The other is the lag of the platinum strip in reaching the temperature to which the last increment of current which it has received will eventually heat it. Since these two factors work in the same direction, their effects will be additive. That is, if the Ardometer could record instantaneously the temperature of any body, there would be a temperature lag due to the time required for the platinum strip to come to temperature. If the platinum strip could come to temperature at once, with the ordinary Ardometer there will be the natural lag of the Ardometer. The lag shown will thus be due to the sum of these two factors.

The lag in heating of the platinum strip will in no way effect the melting point. The total error due to lag is thus reduced to that of the Ardometer. According to the Bacharach Instrument Co. (10) the instrument takes about one second to adjust itself for the last 400° increment of temperatures in the upper ranges. This is about the rate of heating on the fast part of the feed.

on the slower part of the feed the rate of heating is 3-4° per second, and the Ardometer readings should record the temperature almost exactly.

It seems possible that the rate of current rise on the first part of the scale is too rapid to make determinations in this range correct without standardization of the instrument with substances of known melting points. For temperatures where the feed is on the slow part of the screw, there should be no appreciable error due to this cause, in using the graph as illustrated.

However, except for gold, this expected error was not found on the pure substances of known melting point (see table 6). Even in the case of gold the merit of the gold was in some doubt with the melting point likely to be somewhat lower than that of pure gold. Hence it is possible that the Graef Ardometer gives correct readings of the temperature of the platinum strip in all ranges even when the temperature is being raised at a fairly rapid rate.

CHAPTER IV

MELTING POINTS OF SOLIDS

Introductory.

In industry and in the laboratory melting points are required for various types of materials. These may be classed as:

(a) Pure substances, elements and chemical compounds, eutectic mixtures, etc. with sharp melting points.

(b) Mechanical mixtures of powdered materials, coal ash, sewer sludge, clays, etc. for which materials etc. in which it is desired to obtain a formation temperature and not a true melting point.

(c) Physical mixtures, fused alloys, salt mixtures, etc. with a melting point range and no fixed temperature to mark the transition from liquid to solid state.

Various materials and mixtures of these types, the melting point or range of which were known from other sources, have been studied with the 76 Braaf apparatus. The results obtained are shown in tables 5 to 13.

Pure Substances

A number of pure substances, the melting point of which were known to be within the temperature range of

the calibration curve were plotted with the apparatus. The results are shown in Table 6.

Table 6.

Melting Points of Pure Substances.

Substance	Gravimetric Melting Point of.	Gravimetric Melting Point of.	Gravimetric Melting Point of.	Gravimetric Melting Point of.	Reference
Silver	1775	1760	15	(15)	
Gold	1900	1842	-48	"	
K ₂ SO ₄	2320	2370	50	"	
CaF ₂	2494	2512	-17	"	
Iron	2850	2750	+10	"	Oxidizing atmosphere
Fe ₂ O ₃	2850	2750	+10	"	"

* References refer to bibliography.

From the table it is seen that very good melting point determinations can be made on pure substances using the gravimetric and the correction curve, (Fig. 4)

Coal Ash.

A great many melting point determinations of coal ash were made. Table 7 gives the melting points as determined on the 15 coal ashes supplied by Calgary to the Research Council of Alberta. (5)

Table 7.

Melting Point of Coal and Substances.

1	2	3	4
Substance	De Graaf	Bur. of Mines Alberta Resch. Council	
	Melting Pt.	Ash Furnace	Ash Furnace
	°F.	Melting Pt. (6)	Melting Pt. (19) *
		°F	°F
Coal #3	2690-2715	2690-2690	2685
Coal #4	2580-2615	2540-2590	2550
" #5	2745-2820	2710-2760	2685
" #6	2460-2505	2410-2420	2370
" #7	2555	2210-2210	2190
" #8	2605	2370-2760	2685
" #9	2415-2565	2310-2330	2460
" #10	2555-2635	2320-2670	+2685
" #14	2350-2370	2500-2510	2460
" #15	2325-2355	2730-2770	+2685
" #16	2410-2535	2510-2570	2505
" #17	2760	2760-2800	+2685
" #18	265. -2685	2520-2570	2460
" #19	2205	2120-2130	2055

* Private Communication.

Table 7 shows that very good checks can be made between the De Graaf, and ash fusion furnace determinations. The maximum difference shown in the Bureau of Mines Ash Fusion Furnace results (Column 2) in two check determinations, is 90°F. (coal #8). In many cases the difference is 40° or 50°F. In the Research Council of Alberta's (14) check run on the Bureau of Mines

results, the greatest error shown is 30°F., (coal #16). It is seen that the average check which can be obtained with the ash fusion furnace is about 50°F., and in some isolated cases the difference may go as high as 100°F.

The values shown for the De Graaf, in Column 2 on the whole also check within 50°F. The greatest difference (150°F.) is coal #9. The results of #9, #10 and #16 were taken many months apart, and those in greatest error were the first determinations made, so that it is possible that the maximum error which should be obtained in checks by an experienced operator, can be set at 100°F. for the De Graaf, as it was for the ash fusion furnace.

In a comparison of De Graaf Temperatures with the Bureau of Mines average values, the greatest error is in #7, where the De Graaf temperature is 145° too high. The next greatest error is for Coal # 18, with a temperature 110° above the Bureau of Mines average temperature. Both these results may be due to oxidization of iron in the coal and during the progress of the determination. Further, in 10 of the examples illustrated, the De Graaf results are slightly higher than the corresponding ash fusion furnace results. This can also be explained by the fact that since oxidizing

conditions were used in the De Graaf the melting point will be higher due to oxidation of the iron to Fe_2O_3 .

Table 8.

Checks between the De Graaf melting points (8) Laboratory No. 2, and Ash Fusion Furnace Melting Points. (De Graaf results corrected using Figure 3.)

No.	De Graaf		Ash Fusion Method		
	Initial	Final	Initial	Softening	Fluid
	$^{\circ}\text{F}$	$^{\circ}\text{F}$	$^{\circ}\text{F}$	$^{\circ}\text{F}$	$^{\circ}\text{F}$
1	2350	2635	2850	2910	
2	2370	2915	2840	2900	2920
3	2360	2615	2500	2600	2690
4	2440	2765	2190	2470	2570
5	2440	2590	2510	2620	2740
6	2215	2325	2080	2180	2420
7	2165	2215	2000	2060	2210
8	2530	2805	2470	2610	2720
9	2170	2305	2130	2280	2520
10	2270	2450	2330	2520	2650
11	2220	2305	2060	2200	2490
12	2325	2650	2590	2710	2820
13	2260	2665	2540	2670	2890
14	2210	2345	2110	2200	2510
15	2305	2700	2550	2650	2750
16	2250	2435	2180	2340	2550
17	2345	2510	2550	2670	2790
18	2155	2325	2100	2400	2550
19	2100	2130	2000	2040	2130

Table 8 is taken from Selvig's report (8) on the De Graaf apparatus. In this report Laboratory No. 2 is that of the Research Council of Alberta, and their

determinations were made on the instrument on which all this work has been done. Column 1 of Table 8 is the average initial temperature reading, given by Selvig, corrected using the calibration graph, Column 2 is the final temperature reading, similarly corrected.

The results of this table show little beyond the fact that in most cases, the De Graaf readings lie between the initial and fluid temperatures given by the ash fusion method.

Table 9 illustrates the type of checks which can be obtained on the softening point and melting point of coal ash, compared to ash furnace determinations.

The checks on softening points are not very good. Considerable variation can be expected on this point unless attempts are made to correlate a stage of fusion, readily recognized in the De Graaf, with the softening temperature as determined in the ash fusion furnace. This correlation was not attempted, but it is possible that a softening point, as determined with the De Graaf apparatus will be of as much value in estimating the clinker forming temperature of a coal, as the ash fusion softening point, determined according to A.S.T.M. specifications (11).

Table 9.

Comparison of De Graaf and Ash Fusion
Furnace Temperatures

Coal No.	De Graaf Fce.		Ash Fusion Fce.	
	Softening	Fusion	Softening	Fusion
	Temp. from	Point from	Temperature	Temperature
	Correction	Correction	Temperature	Temperature
	Curve	Curve		
	°F	°F	°F	°F
304-30-S9	2365	2540	2597 (13*)	2685 (13*)
309-30-S5	2300	2420	2355 "	2420 "
309-30-S8	2300	2415	2355 "	2420 "
310-30-S8	2420	2575	2550 "	2600 "
314-	2255	2305	2327 "	2415 "
317-31-C	2250	2335	2228 "	2330 "
306-31-C		2130		2060 "
306-31-CC		2140		2280 "
311-31-C		2070		2055 "
316-		2375		2500 "
Coal #9	2345	2565	2270 (8)	2520 (8)
Coal #10	2445	2665	2520 "	2650 "
Coal #16	2355	2565	2340	2550 "
Coal #7	2290	2365	2060	2210 "

* Private Communication.

Orton Cones

Orton Cones are made from mineral mixtures, finely ground to give uniformity, and molded into cones of standard size and shape. The constituents forming the mixture are proportioned in such a manner that when sufficiently heated, the tip of the cone will bend over and reach a level with the base of the cone at the

same temperature in every case, provided the rate of heating is uniform in every case, and also provided the rate be fairly slow.

The melting point of cone material can be determined in the De Graaf apparatus, but the resultant temperature cannot be expected to coincide with the melting points which are published for the various cones. Consequently, several cones were placed in the ash fusion furnace, and melting points determined according to the A.S.T.M. Standard Method (11). The results are shown in Table No. 10.

Table 10.

Comparison of Melting Points of Seger Cones made with Standard Ash Fusion Furnace and with the De Graaf apparatus.

1		2	3	4	5	6
Cone		Ash Fusion Fce.			De Graaf Fce.	
Number		Initial	De-Softening	Nose	Initial	Final
		formation	Point	Over		
		°F.	°F.	°F.	°F.	°F.
Cone	3*($\frac{1}{2}$ Size)	2100	2200	2150	2220	2245
"	5 ($\frac{1}{2}$ ")	2150	2290	2220	2170	2230
"	9 ($\frac{1}{2}$ ")	2290	2435	2413	2275	2380
"	9(Full Size)	2280	2430	2344	2275	2380
"	15 ($\frac{1}{2}$ Size)	2550	2620		2480	2600
"	18	2640-2660			2540	2750
"	9(Fused Sample)				2255	2330

* Contains iron.

In Table 10, column 2 gives the initial deformation; column 3 gives the temperature at which the cone had completely collapsed, that is, it had softened sufficiently to have fallen in at all parts and column 4 gives the temperature at which the tip of the cone had bent over and reached a point on a level with the base of the cone. In only one case does column 4 show the melting point temperature given in tables for this cone. For cone #9, full size, the temperature recorded under "nose over" was taken as specified for the melting point of the cones. This cone melts at 2345°F.

Other temperatures recorded under "nose over" are for cones of half the original height, so the melting points recorded in this column will be too high. They are given in tables as

No. 3	--2138	°F
No. 5	--2201	°F
No. 18	--2714	°F

Of these cones, only #3 contains any iron, and the poor checks for this cone can be attributed to the oxidation of some of the iron while the determinations were being made. De Graaf determinations were made on screened material, 100-150 mesh.

Orton cone materials are very viscous when in the liquid condition. For this reason it is impossible to

obtain a true fusion point on these substances. The initial deformation temperature, and the softening temperature as defined above, are easily recognized in the ash fusion furnace. In the De Graaf furnace the initial deformation temperature is also easily determined being the temperature where the first particle begins to lose its angular outline. On screened samples of 100-150 mesh the final De Graaf apparatus melting point has been taken as the temperature where all the particles have lost their angular outline and formed small rounded spots on the platinum strip, but they do not yet show any tendency to spread. It is thought that with these definitions the final De Graaf temperature becomes comparable with the ash fusion furnace softening point. The checks are very close, in column 2 and 5 and in 3 and 6, the maximum error being in the case of cone #3, where the De Graaf apparatus initial deformation is 120° too high.

Cone #9 (Fused sample) shows a De Graaf melting point determination on the fused material of Cone #9 taken from the ash furnace determination, the melting point of which is shown in the table. It is seen that the initial deformation has been lowered 20°F., the final melting point 50°F. by previously fusing the sample

Slags

Cold metallurgical slags are mixtures of silicates similar to coal ash and urton cones, but the materials have already been fused and thus the intimacy of association of the various substances is much more complete. For this reason multiple fusion point determinations on such substances should show much less variation than those on mechanically mixed components.

Table 11 shows melting points on five different slags.

Table 11.

Melting Points of Slags by the De Graaf Method.

1	2	3
Slag	Melting Point	Flow Point
	°F	°F
Trail Electric Steel Wce.	2090-2090	2180-2150
Trail Lead Smelter	2075-2075	2140-2240
Fuming Furnace Slag	2170-2190	2240-2240
Cu. Slag #1	2105	
Cu. Slag #2	2310	

The fusion temperatures of Table 11 were not checked by ash fusion determinations. The first three have two temperatures shown, the melting point determined in the same manner as the value shown in column 6, table 10.

The temperature was then allowed to rise until spreading of the slag occurred on the platinum strip, and this is entered in column 3, table 11 as "Flow Point". For the Trail Electric Steel Furnace and the Trail Furning Furnace slag this point was fairly definite, but in the case of the Trail Lead Smelter slag, the flow point varied somewhat. From observations on the method of melting, it was seen that the Trail Lead Smelter slag was of a more viscous type than the other two, which probably accounts for the variation in its "flow point". The Furning Furnace slag was also somewhat viscous though less so than the Smelter slag. No appreciable variation in the "flow point" was obtained for this slag. The Electric Steel Furnace slag was quite fluid.

These determinations were made on screened material, 100-150 mesh. One difficulty was encountered, in that the De Graaf has been designed for the higher temperatures of coal ash, and in the range in which these slags fall the rate of melting is too great to admit proper determination of the melting point.

Three synthetic slags were also made from the following compositions:

Table 12.

No.	Composition in Per Cent					
	CaO	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	Na ₂ O
31	37.0	13.0	0.0	42.0		
32	35.3	14.4	7.7	40.2	4.0	
33	32.2	16.2	7.2	38.7	8.0	
34	32.3	17.2	7.2	38.7	4.0	4.0

It should be noted that the composition of slag 32 is 36% slag 31 plus 4% K₂O. The composition of slag 33 is 33% 31, 8% K₂O. Similarly, slag 34 is 33% slag 31, 4% K₂O and 4% Na₂O.

Table 13 gives the melting point of these slags, as determined by both De Graaf and by ash fusion furnace methods.

Table 13.

Melting points of synthetic slag mixture of the Graaf and ash fusion furnace methods.

Slag No.	De Graaf Furnace			Ash Fusion Furnace		
	Initial Deformation	Soft'g Temp. °F	Melt'g Point °F	Initial Deformation	Soft'g Temp. °F	Melt'g Point °F
31		2365	2445	2300	2372	2445
32	2335	2335	2445	2350	2375	2430
33	2315	2355	2445			
34	2290	2355	2460	2270	2360	2365

The ash furnace was used in 1941 to determine in three separate runs in the ash fusion furnace belonging to the Research Council of Alberta. In each case 3 to 4 samples were used for a determination. On slabs 31 cones were made, using dextrin dissolved in alcohol as a binder, and the cones mounted as is done in coal ash work in this laboratory (11). The furnace was shut down when fusion seemed complete. However on examining the cones after the furnace had cooled it was found that these were not completely fused, but had shrunk to such a small volume that their height was not great enough to show above the grooves in the Naolin bases. On slabs 32 and 34, small cylinders were constructed, by compressing the mixture in a small briquette press. The cylinders were about $\frac{1}{2}$ " high, and $1\frac{1}{8}$ " diameter. On these it was possible to observe the true melting point.

Some interesting facts have been gained by a study of Tables 12 and 13. Softening temperatures, or points where the greatest contraction occurs, is the same in almost all cases. The final melting point as determined by the ash fusion furnace is decreased somewhat by the addition of H_2O and Li_2O . In the De Graaf the final

melting point is the same in all cases. This is to be expected, because in the De Graaf fusion furnace what we record is an over-all temperature--produced by the earlier melting particles absorbing the later ones. In the De Graaf, the mixture is spread on the platinum strip. If the ingredients were been pulverized and mixed until the particles are all of microscopic size and each constituent is evenly distributed among the other constituents, the melting point should be the formation temperature for the mixture. This is a very difficult condition to obtain, and usually there are a few large particles of one of the constituents which will show its own melting point, in the De Graaf determination. In this case the addition of lower melting point materials has lowered the Initial Deformation but the softening point and melting point has been controlled by particles in the ratio of the original mixture, glass 31.

CHAPTER V.

DE GRAAF FURNACE

The De Graaf apparatus has proved throughout the major part of these investigations a very tricky instrument, and this is probably because almost all the work was done on silicates or mechanical mixtures of silicate materials where the instrument gives the greatest variations in results. It would seem that the instrument is far from being as bad as it is pictured in the report of Selvig (8). Fitterer and Royer give a much more accurate picture of the usefulness of the instrument, its limitations and the determinations for which it is best suited.

The De Graaf furnace was originally designed for ash fusion work. The A.S.T.M. standard ash fusion furnace is the one which is usually used for this work, because it gives the over-all formation temperature. This point corresponds very well with the temperature of formation of clinker. The De Graaf will not give the exact softening point obtained in the ash fusion furnace, but it will give the temperature at which the first particle begins to fuse, and the point where the

majority of the particles have begun to fuse. This latter temperature corresponds fairly closely with the softening point, and should prove just as useful.

At times, in obtaining the final fusion point of a coal ash, one particle will remain solid after all the rest have fused. Such a particle must be disregarded if checks are to be obtained with ^{the} De Graaf furnace. A particle of this size would not affect an ash fusion furnace determination.

The De Graaf Fusion Furnace should prove useful in coal ash work, although some tests would have to be made in order to choose melting points which would correspond with those obtained in ash furnace work. Each operator would have to determine these himself, by trial and error methods, and learn to recognize the end point which he desires to get.

The instrument is not fool-proof, and requires more care on the part of the operator than the ash fusion furnace, to get check results. In coal ash work it would probably not make a good standard, since it is difficult to define the end points required. Referred to a standard method, as the ash fusion furnace, however it should prove very useful.

On sharp melting point mixtures there is probably no method more accurate. For pure substances and eutectic mixtures it should prove very useful. It should also prove useful for all work on slags. In the laboratory it can be used to determine the temperature at which a slag must be held to enable crystallization to take place.

The calibration curve has been made in a different manner than that given in reports (2), but it is considered correct. Only one part of the curve shows great variation, and the reason for the variation has not been determined. It is possibly not due to any inaccuracies of the De Graaf itself and the curve is probably correct.

Sufficient examples of applications of the De Graaf have been given to illustrate its usefulness and check the calibration.

To the person who has to use the instrument for the first time, the De Graaf will present many difficulties. No better reference than Witterer and Royer's report (2) can be found to instruct him in the manipulation of the instrument, and to give confidence in the results which will be obtained.

PART II.

CRYSTALLIZATION IN SILICATE BELTS; INTER-
PRETATION OF CRYSTAL STRUCTURE DE-
VELOPED, AND DETERMINATION OF
MINERAL IDENTIFIERS BY
POLISHED SECTIONS AND
BY THIN SECTIONS.

CHAPTER I

INTRODUCTORY AND PREVIOUS WORK.

Introduction.

As has been mentioned in the introduction, the work of the following pages describes the preparation of some crystalline slag materials, both synthetic and real, for study by microscopic methods, and an interpretation, in some cases rather abbreviated, of the crystal phases which were obtained. The work is essentially introductory in nature, and goes little farther than to point out a direction in which the studies of these slags may take. In some respects it is new, in that a study of polished sections, etched by hydrochloric and hydrofluoric acid, have been interpreted in the light of slag composition. In some instances these interpretations have been supported by a study of thin sections of the slags concerned.

Previous Work.

Silicate melts have been studied from two different points of view. On the one hand they have been used by certain investigators to aid in the interpretation of mineral occurrences in igneous rocks. By others they

have been employed to help in understanding conditions met with in industry, especially in the branches of pyrometallurgy and ceramics.

Geological Approach.

Beyschlag, Vogt and Krusch (15) state that a molten silicate solution is to be regarded in general as a mutual solution of a series of components chemically identical with those minerals which crystallize out at solidification. Even the components which form mix crystals are to be regarded as independent components in the magmatic solution. On cooling minerals, either a solid solution or definite compounds may form with lowering of temperature down to the eutectic point. The first mineral to crystallize out will be the one which is in excess of the proportions required for a eutectic. In the fluid condition, silicates are freely soluble in one another. Some oxides also are soluble in the molten silicate solution, but separate out on cooling; i.e. the spinels.

Bowen, Schairer and Posnjak (16) published a paper dealing with the CaO.FeO.SiO_2 system which is of interest to lead and copper metallurgists. They state that the slags of lead and copper smelters are composed

essentially of these three constituents, and by means of a three component diagram they showed that it is possible to derive some conception of the properties of the slag in either the liquid or solid state.

As a practical illustration of the use of a knowledge of mineral composition, these authors discuss the action of slag on silica refractories.

Metallurgical Approach

The groups of minerals occurring in the metallurgical slags as determined by various workers, may be summarized as,

- (1) Olivines -- Fayalite, forsterite monticellite.
- (2) Pyroxenes -- Hedenbergite, diopside, augite,
calcium orthosilicate, (wollastonite)
- (3) Melilites -- Gehlenite, akermanite.
- (4) Spinel -- magnetite, Gahnite
- (5) Felspars -- Anorthite.

McLellan (17) dealing with the petrographic study of lead and copper furnace slags showed that the investigation of lead and copper furnace slags involves the study of the possible compounds resulting from fusions containing SiO_2 , Al_2O_3 , CaO , ZnO , sulphur and

the oxides and ferrites of iron. He pointed out that while slags of iron metallurgy may be considered as "dry melts", lead and copper slags are charged with nascent sulphur and the oxides of sulphur and that these may be considered as similar to the superheated steam, chlorine and other mineralizers of igneous rocks.

McLellan says that the presence of this nascent sulphur renders the iron bearing compounds easily fusible since they are almost completely reduced to the ferrous condition. His method of study of slags is: (1) to accumulate all available information on the components pertaining to the slag; (2) to determine by analytical methods the mineral constituents existing in commercial slag; (3) after the above studies are complete, to investigate by synthetic methods the conditions of formation and physical properties of the slag. He presents pictures of thin sections of industrial lead and copper slags, which are in his own words, "designed to simplify the course to be followed in future slag studies by synthetic fusions."

Oldright and Miller (18) state that it is questionable whether what has been learned from a study of frozen, slowly cooled samples can be applied to that

occurs in a molten magma or solution. They show that taking ^{as} an example iron, which can exist in either the ferrous or ferric state, it would be necessary to obtain sections from the top to the bottom of a slowly cooled sample to get any quantitative idea of the amount of iron in the ferric state in the original melt.

McCaffery's Work.

McCaffery has studied the mineral entities occurring in Iron Blast Furnace slags. He and his co-workers (19, 20) give a method by means of which the information obtained by a knowledge of the mineral composition of a slag, can be used to predict and correct adverse conditions in the Blast Furnace. They were concerned chiefly with the four component system $\text{CaO}.\text{MgO}.\text{Al}_2\text{O}_3.\text{SiO}_2$ and make use of the equilateral tetrahedron to determine the minerals which will crystallize from a mixture of these oxides. McCaffery's tetrahedron for this system is reproduced in Figure 1. The front left corner of the tetrahedron represents 100% silica, the front right 100% alumina, and the top 100% magnesia. The principal compounds or mineral entities are named, and three of the internal tetrahedra are outlined by shaded planes. The particular tetrahedron, diopside, akermanite, calcium

bisilicate and anorthite encloses the composition of the synthetic slags discussed later.

Such a diagram shows that there are ranges of chemical composition where a small change in quantity of a component produces a great change in the mineral types. According to McCaffery, this explains why one day a furnace may be working well, and the next day be off no matter what other operating conditions are changed in an effort to correct it.

McCaffery (20) preparing synthetic slags for viscosity determinations, used mineralogical instead of chemical compositions as a basis for his slag mixtures. The mineral compounds were made from pure oxides of lime, magnesia, alumina and silica. After each melt the slag was ground, sampled and analyzed to determine the percentage of each constituent oxide. Each compound was fused and analyzed and additional ingredients added until a homogeneous mixture was obtained. The final analysis of his melts corresponded with the percentage composition of the minerals as shown in Table 1.

To make a slag of any desired mineralogical composition, McCaffery had only to weigh out the required portion of each mineral prepared as above, to mix these and heat them until fusion was complete.

Table 1.

Chemical and Mineralogical Composition of
Synthetic Mixtures (after McCaffery).

Mineral	Chemical Formula	CaO-MgO%	Al ₂ O ₃ %	SiO ₂ %
Akermanite	2CaO.MgO.2SiO ₂	41.14	14.79	44.07
Anorthite	CaO.Al ₂ O ₃ .2SiO ₂	20.16	36.64	45.19
Calcium bisilicate	CaO.SiO ₂	48.28		51.72
Dionside	CaO.MgO.2SiO ₂	25.90	18.62	55.48

CHAPTER II

PREPARATION AND CRYSTALLIZATION OF THE SLAGS.

Synthetic Slags.

The group of minerals given in Table I formed the basis for the manufacture of the synthetic slags dealt with in this chapter. The materials however, were proportioned according to the oxide components, and not according to the mineralogical components, but nevertheless some of the resulting crystalline entities developed have been shown to coincide with those given in the table.

Two synthetic slag melts were prepared, of composition shown in table 2.

Table 2.

Composition of Synthetic Slags

Composition	Slag A Slag B	
	%	%
Chemical		
CaO	25.67	31.81
MgO	6.55	11.78
Al ₂ O ₃	9.16	6.11
SiO ₂	48.62	50.90
Mineralogical		
Aegirinite	25	16.66
Anorthite	25	16.66
Collastonite	25	16.66
Dioptase	25	50.00

The mineralogical composition given in the tables are based on the work of Coffey (13, 20).

Slag 1.

A known weight of the mixture of the chemical entities was fused in a small nickel crucible in the ash fusion furnace illustrated in Figure 2, Part 1. The melting point of the mixture was known from Coffey's work to lie below 2370°F . The furnace was therefore heated to 2450°F . or approximately 200°F . above the melting point to ensure complete fusion of the melt. The temperature was then lowered rapidly to 2400°F . and within the temperature range 2350°F - 2300°F . for three hours, and between 2250°F - 2200°F . for five hours, and then allowed to cool with the furnace from 1900°F .

The resulting slag was found to be a coarse crystalline mass (Figure 3).

A cross section of the mass showed evidences of segregation (Figure 4) by the differentiation of the liquid during cooling or differences in degree of crystallization due to more rapid cooling at the top of the melt.

The crucible showed appreciable corrosion. Weighing of the fused mass showed 4.5% nickel.

Slur 3.

A known weight of the mixture of the chemical entities was placed in a graphite lined fire-clay crucible. The graphite lining was prepared by mixing 100 mesh ground electrode carbon with 10% acetone solution as a binder, and coating the inside of the fire-clay crucible with about 1/8" layer of this mixture. The crucible and its lining was subsequently dried at 2200°F.

The melting point of the clay mixture was known from McCaffery to be approximately 2200°F. The melt therefore was subjected to a temperature above 2200°F. For one hour, the maximum temperature reached being 2420°F. The temperature was then lowered relatively quickly to reach a temperature of 1950°F. In one hour from which temperature the melt was allowed to cool with the furnace.

The resulting material was found to be very crystalline. Particles of SiO₂ remained visible in the mass, indicating that time was not been allowed for complete liquifaction of the original powdered mixture.

The graphite lining of the crucible was found to have partially burned away, but sufficient remained to

protect the slag from contamination by the metal and the crucible was in such good condition that a second melt could be made in it.

Metallurgical Slags

Several types of slag are obtained from the Trail Smelter of the Consolidated Mining and Smelting Company of Canada. Partial analyses of these slags are shown in Table 5.

Table 5.

Composition of Metallurgical
Slags from the Trail Smelter.

Chemical Composition	Slag A	Slag B	Slag C
Fe	5.0	20.0	25.4
Zn		10.0	5.1
Mn	10.0		
CaO	2.0	10.4	11.0
SiO ₂	60.0	19.4	25.4
Al ₂ O ₃		6.0	0.8

Slag A -- Electric Steel Furnace slag, analysis by C.M. & S. Co.

Slag B -- Lead Blast Furnace slag, analysis by the author.

Slag C -- Zinc Smelting Furnace slag (21), analysis by C.M. & S. Co.

No attempt has been made to estimate the mineralogical composition from the chemical composition, but the

work of McElroy and of Gurnett and Miller indicate the presence of magnetite and other minerals in slags A and B.

As received, slag A was dark in color, and gave no indications of the presence of crystalline mineral entities. This was to be expected from the high silicon content and the relatively rapid cooling from the high temperature to which it had been subjected in the electric furnace. Slags B and C were dark colored, stony, and showed some incipient crystallization.

Attempts were made to crystallize these slags in a manner similar to that outlined under synthetic slags, using the granite lined crucible in all cases. They were much more difficult to crystallize, and only after several trials was it possible to obtain crystals of any size.

Slag C.

The Electric Steel furnace slag was heated to 2800° C. and brought down fairly rapidly to a temperature of 2065° C. The crucible containing the slag was then transferred to a muffle furnace at a temperature of 2065° F. and cooled gradually to 1775° F., over a period of 50 hours.

The resulting slag was a brown stony mass with

numerous gas cavities. There was no macroscopic appearance of crystallization, but its crystalline character was clearly observable in polished sections.

Slag D

The Lead Blast Furnace slag was crystallized in the graphite lined crucible in a gas-fired muffle furnace. Temperatures, observed by a chromel-alumel thermocouple and potentiometer indicator were held between 2000° - 2050° for two hours, and then decreased to 1775° over a period of five hours.

The resulting slag was a dark porous stony slag, quite crystalline in appearance, although not as coarsely crystalline as the synthetic slags.

Slag E

The Trail Smelter Furnace slag was heated in the gas fusion furnace to a temperature of 2320°F . and cooled over a period of three hours to 2250°F . when the furnace was shut off. The resulting slag was largely a glass but contained some minute crystals indicating that the first crystals had begun to separate at about 2250°F . Surrounding the slag button, in a thin sheet between it and the graphite lining was a layer of metal which when

peeled off, weighed 1.5 grams. The strong reducing atmosphere of the furnace had resulted in some of the metallic oxides in the slag being reduced to free metal.

Two more furnace runs on the same slag mixture at progressively decreasing temperatures were necessary before a crystalline slag was obtained. In each case a layer of metal was reduced from the slag, and the melting point of the slag reduced by the loss of this component from the slag.

Analysis of the reduced metal showed it to be essentially metallic iron with minor amounts of copper, zinc and lead. The weight of metal produced closely approximated the total weight of iron in the original slag. The remaining material showed a fairly crystalline slag, but it had no longer the composition of the Furnace Furnace slag.

Fragments of the crystalline masses were mounted for microscopic study by both reflected and transmitted light. The results of these examinations are given later. They clearly show that the methods adopted have in the case of all the slags studied developed a definite crystalline character with the mass. It is important to notice that as complete crystallization developed in synthetic slag

with a relatively short period at the crystallizing temperature as in slag A under prolonged cooling. On the basis of this result it was assumed that a cooling rate intermediate between those of A and B would prove satisfactory for most industrial slags. Results on the metallurgical slags in part confirm this, although possibly a more complete crystallization could have been obtained by a somewhat slower cooling.

CHAPTER III

MINERAL CONSTITUENTS OF THE SLAG

Introduction

Mineral determination by microchemical tests on polished sections is an accepted method for opaque minerals but the method has not been applied to the rock forming minerals as far as the writer is aware. It seemed possible that a similar method might be applied to the rock forming minerals also, and attempts have been made to determine the mineral species present in some of the slags by this method.

The processes of mineral crystallization from the molten slag must follow the normal principles of solidification. In any mixture of four (or more) components the crystal entities forming on solidification must do so either in sequence or contemporaneously. Crystallization of a mixture will normally take place over a temperature range and in a definite sequence depending upon the relative amounts of crystal forming constituents present. Contemporaneous crystallization will only occur if the constituents are present in just the right proportions to give the eutectic concentrations. Other-

wise one substance will come out of solution and thus enrich the remaining liquid towards the concentration of the first eutectic. One or more eutectics will form as the concentrations of the liquid change with crystallization of the pro eutectic substances.

The first mineral (or crystal) entity crystallizing out of a slag melt will be freely suspended in the liquid mass. If it is a relatively infusible substance it should readily assume its normal crystal habit developing as idiomorphic crystals. If the crystalline substance is lighter or heavier than the parent liquid some segregation may be expected particularly if the mass is held at a suitable temperature for some period of time to allow the force of gravity to act.

Simultaneous crystallization of two components may occur in two ways, (a) as mix-crystals or solid solutions and (b) as an eutectic. The eutectic may be formed of the primary constituents or of solid solutions of these in one another. In either case if the temperature of formation is high relative to the most fusible mixture of the components of the melt, the tendency should be for the two components so crystallizing to form more or less idiomorphic crystals and the characteristic intimate

crystallization of an eutectic may not be very obvious. At this stage in the solidification the mass will consist of idiomorphic crystals of the first component to crystallize suspended or floating in a mushy mass composed of residual liquid and small, possibly idiomorphic crystals of two components, one those of primary constituents and the other of the constituent of next higher melting (or freezing) point.

Further cooling should result in the crystallization of the remaining liquid to a eutectic either with or without crystallization of other pro-eutectic substances. Again these eutectics may be composed of principal constituents only or may be solid solutions of these constituents one in the other.

Any solid solutions formed during the processes of solidification may or may not break down on subsequent cooling below the solidus with the formation of new crystal entities within the parent solid mass. Obviously, slow cooling below the solidus should promote and rapid cooling retard this break down.

It must also be borne in mind that at any stage in the solidification conditions may be right for reaction between some of the previously crystallized solids and

the liquid in contact with them with the development of new solids by reaction (peritectic reactions). These may form complete new substances, solid solutions or chemical compounds, more or less pseudomorphic after the original solid, or develop a reaction ring around the pre-existing crystals.

Structures to be expected in polished sections can be summarized as follows,-

1. More or less idiomorphic crystals of the first component.
2. Mixtures of idiomorphic or hypidiomorphic crystals of two (or more) components characterized by a more or less uniform grain size.
3. Eutectic mixtures showing the typical granular, fibrous or platey structures.
4. Idiomorphic or hyp-idiomorphic crystals pseudomorphs after a pre-existing crystal.
5. Idiomorphic or hypidiomorphic crystals with distinct reaction ring.
6. Idiomorphic, hyp-idiomorphic or allotriomorphic crystal outlines showing secondary structures developed due to the break down of original solid solutions.

Relief polishing or suitable etching should outline these structures readily but the determination of the particular crystal entities forming the structures would have to be determined by distinctive physical properties and/or more or less specific microchemical reactions.

Confirmation of the determinations in the case of mineral entities might be made by thin section petrographic studies.

Specific properties which may reasonably be expected to differentiate mineral species in polished sections are as follows,-

1. Crystal habit and interior structures such as cleavage, etc.
2. Color.
3. Hardness.
4. Fusibility (Melting Point or Fusion Point).
5. Density or specific gravity.
6. Solubility in reagents (etch effects).

Representative pieces of the slags crystallized as outlined in Chapter II were selected for microscopic examination and possible mineral determination both by polished section and thin section methods. A complete determination was found to be impossible largely due to difficulties in making satisfactory thin sections. The solid slags were brittle and the crystals or fragments of them tore out of the matrix before the mineral section was sufficiently thin to permit good petrographic determinations. Polished sections prepared by first impregnating the specimen with bakelite varnish and then

mounting in bakelite have proved more satisfactory. Polished and suitably etched these sections have revealed practically all the structure types enumerated above. Selective etching has indicated the probable minerals present in some cases and in most cases these have been confirmed by thin section petrographic examination.

Slag "A"

As previously described this synthetic slag was prepared from materials which, according to McCaffery (20) were in proportions to develop the four mineral entities wollastonite (or pseudo-wollastonite), akermanite, anorthite and diopside. It could be expected that some, if not all, of these minerals would be developed in the slag.

Physical properties of these minerals which should aid in determinations by micro-chemical tests on polished sections are shown in Table IV.

Macrostructure of a vertical cross section of the melt of slag "A" has been shown in Figure 3 (31). There is distinct evidence of segregation. Large lath shaped or prismatic crystals embedded in a structureless groundmass occur at the top of the section, while a

granular mass with, perhaps, occasional lath shaped crystals forms the bottom portion.

Table IV.

Physical properties of presumed mineral components of slag "A".

Mineral Properties	Wollastonite	Kermanite (Meliinite)	Northite	Dionside
Crystal form	monoclinic	tetragonal	triclinic	monoclinic
Cleavage	pinacoidal	basal	basal & pinacoid	prismatic
Hardness	4.5 - 5.0	5.0	6.0 - 6.5	5.0 - 6.0
Fusibility	4	3	4.5	4
Spec. Grav.	2.8 - 2.9	2.9 - 3.1	2.7	5.2 - 5.3
Sol. in HCl	readily	soluble	difficult	Insol.

The large lath shaped crystals, etched with 5% solution of hydrochloric acid are shown in Figure 4 at 100 diameters. Two types of mineral substances are indicated. Crystals (1) are more holocrystalline, show greater relief and are less marked by the polishing scratches than crystals (2). They are also somewhat less darkened by the etching reagent. They are thus less fusible, less soluble in HCl and harder than crystals (2). Both show internal structures with a marked parallelism to the long axis of the lath. Elsewhere in the section

crystals in thin sections similar to those (1) show the internal structures shown in Figure 2. This is very definitely the so-called "peg" structure typical of the melilitite and would indicate that crystal type (1) at least is of the melilitite group and hence microcline.

Differences in the crystal types (2) and (3) have been outlined. On the other hand there are very points of similarity. Scattered throughout the slides are crystal aggregates of the same "F" type, some of crystal type (1) and others of type (2). Etched with HF acid different characteristics to some extent disappear as shown in Figure (6). Both types are attached with the reagent and the only apparent difference is a more pronounced parallel banding in type (1). It may be that the dissimilarities exhibited in Figure 4 have been caused by sectioning line or etch in different crystallographic directions and the polished section is thus made to suggest two different mineral entities.

A thin section, under crossed nicols and at 100 diameters is shown in Figure 7. Only one type of crystal is observable. This was found to be radial and positive and may be determined as either pseudo-wollastonite (a form of wollastonite stable above 1150°C) or anorthite.

shown in conjunction with the "X" structures indicated in Figure 3 it may be assumed that these large orthorhombic crystals are crystals of anorthite. It should be pointed out, however, that in the "X" structure is the proportions of CaO in the slag forming constituents of the melt tend to decrease the amount of this mineral although anorthite is the principal forming mineral of these two.

The structure also occurring at the center of the melt as shown in Figure 3, shows two types of structure as indicated in Figures 4 and 5. Figure 7 shows an XOI etched polished section of this portion of the melt at 100 diameters. Small idiomorphic crystals, prismatic in shape and frequently euhedral, are indicated in a structureless groundmass. Some of the crystal boundaries are definitely etched in outline; others have a smooth prismatic form with thick dark boundaries. The latter type is relatively hard so that it stands out prominently while the former is softer, showing the relative hardness and is somewhat more deeply attacked or etched in the etching process. The short, prismatic, hard crystal resembles lopsided while the others have most of the characteristics of the large prismatic crystals shown in

Figures 4 and 5. The etched groundmass which is
 confirmed by the entire cross section, by the basal
 section of a tetragonal crystal and also by
 is the only tetragonal crystal likely to be present in
 the mixture. The section probably represents the sim-
 ultaneous crystallization of almandine and diaspore
 with the structureless groundmass a chilled solution of
 the remaining portions of the melt. The groundmass may
 be a fine grained quartz-silica eutectic with the structure
 not brought out by the etch attack.

A thin section of this portion of the melt is
 shown, at 100 magnifications, in Figure 6. The isotropic
 groundmass suggests a chilled glass. No distinct con-
 vergent polarized figure could be obtained on the small
 crystals although most of them were distinctly uniaxial.
 A few were biaxial. The rectangular prisms suggest
 oblique sections of a tetragonal crystal and the al-
 mandine is again indicated.

At a somewhat greater depth in the melt, the struc-
 ture shown in Figure 9 was obtained. Stubby, prismatic
 crystals apparently hard and relatively brittle, with
 numerous irregular black check cracks are imbedded in
 a fine grained distinctly eutectiferous background.

The eutectic is fibrous in structure and carries a distinctly greater proportion of one component than of the other or others. This component, the white substance, is in many ways similar to the structureless groundmass of Figure 7 and being a component of a eutectic, cannot be a glass. It may be a solid solution. This structure was not obtained in the thin section of this portion of the melt and no petrographic determination of the mineral constituents could be made. The general appearance in the polished section is strongly suggestive of crystals of diorite and gabbro in a multiple component eutectic groundmass.

The structures shown in Figure 10 were relatively abundant in the lower portions of the melt. Figure 10 shows an orderly arrangement of two components in parallel bands, presumably developed on the same structural skeleton, a columnar crystal or dendrite. The wider bands stand out in relief and are characterized by numerous irregularly spaced black cross bands. Occasional minute granular particles within the broader bands suggest the "pe" structure and the general appearance of these portions of the structure resembles the large crystals of Figure 4. The alternating narrow bands are structureless

and practically free from the black cross banding. It is suggestive of the white component of the eutectic shown in figure 9.

Figure 11 represents a thin section, under crossed nicols and at 100 magnifications, of a similar though not identical structure. Parallel extinction in the alternate bands suggests a continuity of crystal growth. No determination could be made of the mineral components present.

Slag B.

The mineral composition of slag B is 50% diopside, with the remaining minerals akermanite, wollastonite and anorthite, present in equal proportions. Polished sections of this slag are given in Figures 12 and 14. They show chiefly pre-eutectic crystals of a shape much like the lath-shaped crystals of slag A, in a eutectic ground mass. A petrographic determination of a fragment of one of these crystals showed it to be uniaxial and positive so that it is possibly akermanite or pseudo-wollastonite. No determination of the composition of the ground mass was possible.

slag C.

As has already been mentioned, the Electric Steel furnace slag as received was a glass without any indications of crystallization. After crystallization treatment, a polished section of the slag unetched appears as in Figure 15.

Two types of crystals appear in the figure; one smaller and irregular in outline (1), the other faintly in the background as much larger idiomorphic crystals (2) with an apparent monoclinic or triclinic habit. The first crystals cut across the second in an irregular manner, and undoubtedly formed almost completely before the second crystals began to appear. No etch effects were attempted in this specimen to bring out the nature of the second group of crystals.

Thin sections of this slag gave an entirely different structure. The crystals (1) in Figure 14 appeared much the same and were easily determined as of the olivine group, probably tephroite (Mg_2SiO_4). The only other constituent seen in thin sections was a group of crystallites, whose composition could not be determined.

The bright oval spots scattered throughout Figure 15 are due to metal which remained in the slag, and could

be seen in the specimen as received. The groundmass in this slag is probably a glass.

Slag D

This slag and the next to be discussed, (Slag E) are products of the Lead Smelter at Trail, B.C., and hence have certain characteristics in common. Figure 16 shows a polished section, unetched, of slag D as received. Only one type of crystal appears, which according to McEllan (4) and Aldright and Miller (5) should be spinel. The groundmass is non-crystalline. There are indications of the growth of a second type of crystal, but these appear chiefly as small crystallites branching off a central spine. Pits show the mass was somewhat porous. Some globules of metal also appear in the polished section.

After holding the slag at a temperature close to its melting point for some time, it was found the crystalline phase had not been appreciably increased (Figure 17). More metal had been reduced and possibly more spinels had developed, but these were smaller and more widely distributed throughout the mass of the solid.

Spinel is held in a slag in solution. On cooling the slag the solubility for spinels decreases and they crystallize out. In Figures 16 and 17 spinels which have

separated out from the slag in this manner, show an internal structure indicating a subsequent breakdown of a previously formed solid solution.

Slag E

Slag E is closely related to slag D, and the polished section of the slag as received (Figure 18) appears very much like Figure 16. Exactly the same constituents are shown in both figures. This is to be expected, for except for the zinc oxide and lead oxide which have been removed (21) in slag E, its composition is the same as slag D. Zinc oxide occurs in slags largely in solution, and as such will not affect the first crystals to form in slag E.

In the treatment of this slag to promote crystallization, much of the iron was reduced, leaving the slag fairly clear and glassy, and this slag had to be subjected to further treatment to promote crystallization. The resultant crystalline slag shown in Figure 19, is thus not comparable with that shown in Figure 18. Figure 19 indicates that one type of crystal has formed in the slag, in small quantities, and the remainder has crystallized as a eutectic. A thin section of this slag showed chiefly a eutectic, with the crystal phase present but only in

minute parallelograms which could not be determined. They are probably olivines, the minerals most likely to crystallize out under these conditions.

CHAPTER IV.

CONCLUSIONS.

A method of crystallization treatment for the production of crystal structures in slags has been indicated and some of the crystal structures which may be expected from such a treatment have been shown.

It has been found possible to develop crystallization in synthetic and metallurgical slags, including siliceous high temperature slags of the Electric Steel Furnace. Crystals so produced are clearly observable in polished sections after treatment with suitable etching reagents. Crystal structure so developed appears characteristic, and is in many ways similar to that seen in petrographic studies.

Determination of the minerals formed, on a basis of polished sections alone, has not been proved, largely through lack of technique in making thin sections of the slag to confirm the deductions made on the polished sections, but it would appear that crystal habit, internal structure, hardness, and etch effects can be used to make fairly definite mineral determinations in polished sections.

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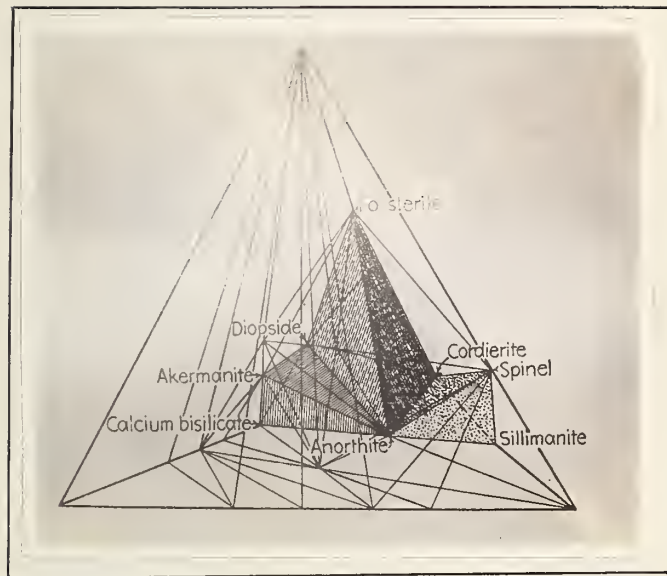


Figure 1.

McCaffery's Tetrahedron for Lime, Alumina,
 Magnesia and Silica showing three of
 the internal tetrahedra.

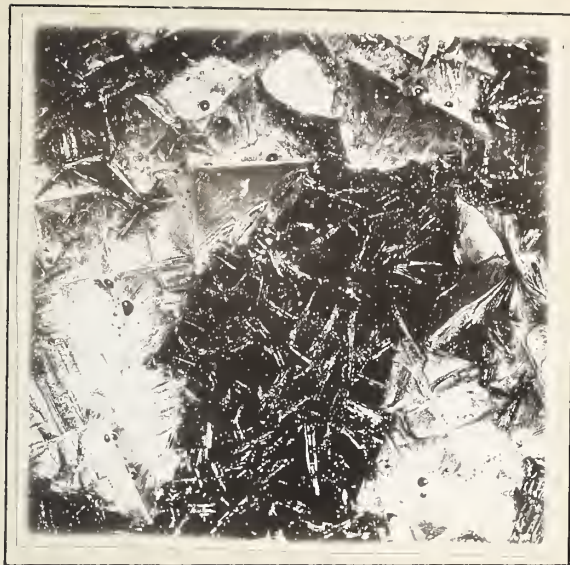


Figure 2.

Surface appearance of slag "A". X 40



Figure 3.

Vertical cross section of slag "A"
Etched with 5% HCl. X 20



Figure 4.

Polished Section of top portion of melt of slag "A"
HCl etch. Mag. 100 X.

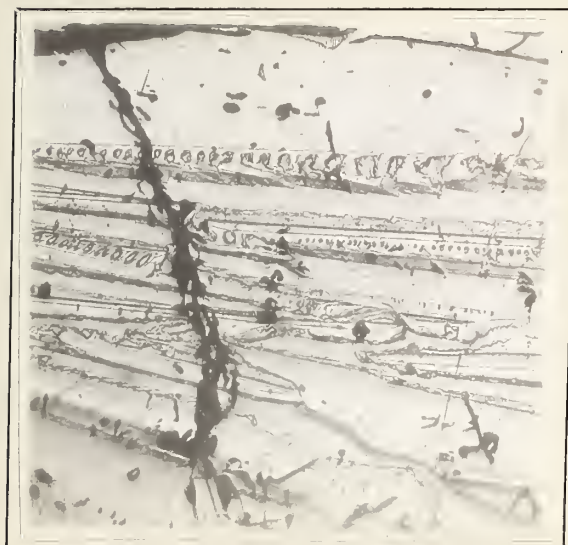


Figure 5.

Polished section of top portion of melt of slag "A"
showing "peg" structure in lath-shaped crystals.
HCl etch. Mag. 100 X.



Figure 6

Same area as Figure 4.
HF etch. Mag. 100 X



Figure 7.

Thin section of top portion
of melt of slag "A"
Crossed nicols. Mag. 100 X.



Figure 8

Central portion of melt of slag "A"
Polished section.
HCl etch. Mag. 100 X.



Figure 9

Thin section of central portion
of melt of slag "A".
Crossed nicols. Mag. 100 X.



Figure 10.

Polished section central portion
of melt of slag "A".
HCL etch. Mag. 100 X.

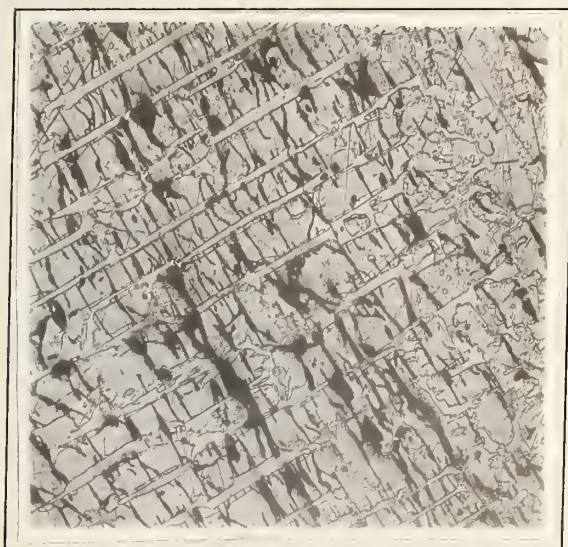


Figure 11.

Polished section of bottom portion
of melt of slag "A".
HCL etch. Mag. 100 X

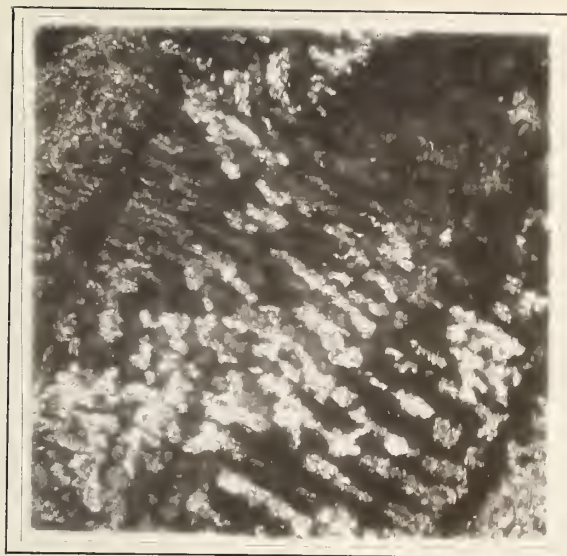


Figure 12

This section of bottom portion
of Slag "A"
Crossed nicols Mag. 100 X.

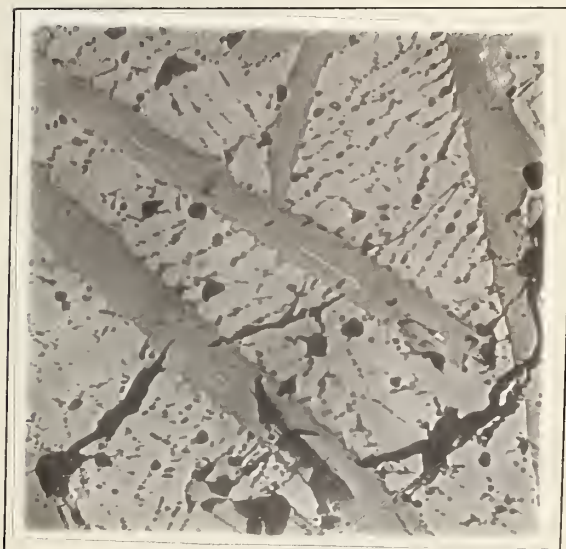


Figure 13

polished section of Slag "B"
Not etched. Mag. 100 X.



Figure 14

Polished section of Slag "B"
HCl etch. Mag. 100 X

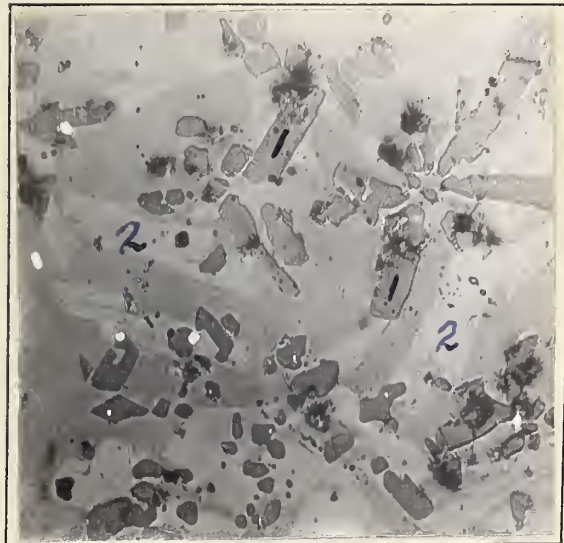


Figure 15

Polished section of slag "C"
Not etched. Mag. 100 X



Figure 16.

Polished section of slag "D"
Not etched. Mag. 100 X.



Figure 17.

Polished section of slag "D"
HCl etch. Mag. 100 X.

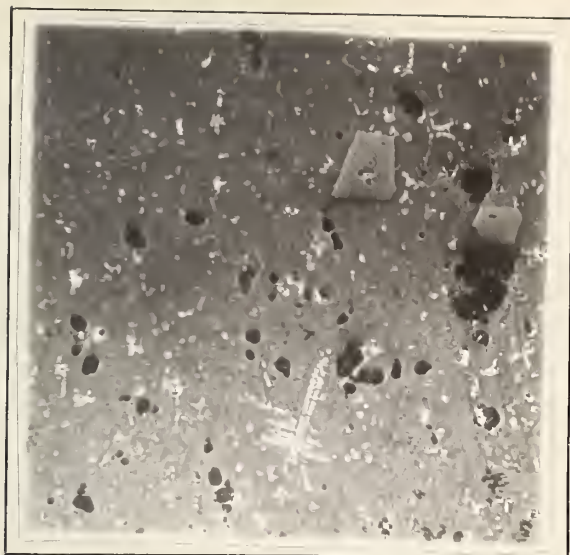


Figure 18

Polished section of slag "L" as received
Not etched. Mag. 100 X



Figure 19.

Polished section of slag "L" recrystallized.
HCl etch. Mag. 100 X.

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